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**Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals**

**Sub-Committee of Experts on the Transport of Dangerous Goods**

**Forty-seventh session**
Geneva, 22 – 26 June 2015
Item 2 (c) of the provisional agenda
**Explosives and related matters: Review of tests in parts I and II of the Manual of Tests and Criteria**

# Manual of Tests and Criteria

# Recommendations for improvement of series 8 (c) Koenen Test

**Transmitted by the Institute of Makers of Explosives (IME) and the Australian Explosives Industry Safety Group (AEISG)**[1]

## Introduction

1. At the thirty-ninth session of the Sub-Committee, the Working Group on Explosives discussed issues of difficulty in conducting tests outlined in the Manual of Tests and Criteria and recommended to the Sub-Committee[2] that the Working Group on Explosives conduct a review of the tests mentioned in Parts I and II of the manual with a view to:

(a) Better defining the specifications of the tests;

(b) Better defining the tolerances associated with those specifications; and

(c) To remove any unnecessary or over-specifications.

2. The Sub-Committee agreed that this work should be carried out[3].

[1] In accordance with the programme of work of the Sub-Committee for 2015–2016 approved by the Committee at its seventh session (see ST/SG/AC.10/C.3/92, paragraph 95 and ST/SG/AC.10/42, para. 15).

[2] Informal document INF.58 (39th session), para. 13

[3] ST/SG/AC.10/C.3/78, paras. 24 - 25

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3. As part of this initiative, the Koenen Test 8(c) was subject to a review of its origin. Over the years, tests carried out by testing bodies and industry showed that the steel of the tube softens and weakens considerably before any apparent response of the ANE[4] to the effects of heating. Typically the time for ANEs to exhibit any reaction (other than oozing out from the orifice) under intense heat is an order of magnitude longer than those substances evaluated by Koenen and Ide in the 1950s and for which the test was developed. This prolonged heating can lead to degradation in the strength of the steel tube from thermal softening and also from oxidation through contact with the hot AN solution contained in the tube, the decomposition products of which include nitric acid.

4. AEISG has already submitted a paper proposing that the orifice diameter be set to 2 mm for the test and 1.5 for the calibration of the tube[5]. This proposal was considered and endorsed by the Working Group on Explosives[6], approved by the Sub-Committee at its forty-fifth session[7] and forty-sixth session[8], and approved by the Committee at its seventh session[9].

5. The discussion that follows will show that the extended times seen with applying the Koenen test to ANEs, which was developed for molecular explosives, will result in changing the property of the steel tube and hence influence the result since the test becomes one of not only the substance within the steel tube, but also of the steel itself.

## Discussion

6. Over the last 30 years ANEs have become the predominant feedstock in the manufacture of bulk explosives replacing molecular explosives, which were the substances used when Koenen and Ide developed their test. The lower sensitivity, higher thermal stability, and their ability to be manufactured into bulk explosives have made ANEs become the commercial feedstock of choice

7. The paper by Koenen and Ide[10] published in 1956 was studied to determine the conditions under which the test was carried out during its development and later incorporation into the Manual of Tests and Criteria. An extensive report on this review was published in 2011[11].

8. Tests carried out by testing bodies and industry showed that the typical time to reaction for ANEs was several minutes, in stark contrast to the substances tested by Koenen and Ide, which typically exhibited reaction times of 2 to 20 seconds for Group I substances, and up to 56 seconds for Group II[11]. At the time of Koenen and Ide's research, ANEs did not exist. It was further shown in that study that the 'useable' time, i.e. the time beyond which the steel would be 'softened' would be as short as 25 seconds for inert solids such as sand where the contents did not wet the inner surface of the tube.

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[4] The abbreviation ANE will be used to denote those ammonium nitrate emulsions, suspensions and gels conforming to UN 3375

[5] ST/SG/AC.10/C.3/2014/11

[6] Informal document INF.61 (45th session), para. 9

[7] ST/SG/AC.10/C.3/90, para.20 and ST/SG/AC.10/C.3/2014/73, Part II, Section 18 (pp. 45 – 46)

[8] ST/SG/AC.10/C.3/92, para. 8

[9] ST/SG/AC.10/42, para.12

[10] Dr. H. Koenen und Dr. K.H. Ide, "Über die Prüfung explosiver Stoffe. III. Ermittlung der Empfindlichkeit explosiver Stoffe gegen thermische Beanspruchung in einer Erhitzungskammer mit verschiedenen definierten Öffnungen (Stahlhülsenverfahren)", *Explosivstoffe*, Nr. 6, Juni 1956, pp. 119-125 und *Explosivstoffe*, Nr. 7, Juli 1956, pp. 143-148

[11] Informal document INF.53 (39th session)

9. The type of steel used for the tube that contains the substance is DC04 steel sheet. The properties of this steel as a function of temperature are shown in the annex to this document. At the time of incorporation of the Koenen Test into the Manual of Tests and criteria, the commercial explosives were very similar to those used for the development of the test. From the chart it can be seen that the yield stress of that steel for an effective plastic strain of 0.20 drops from 550 MPa to 350 MPa when heated to 315°C, showing that this type of steel does not retain its strength on heating.

10. The test was developed by Koenen and Ide for substances more reactive than ANEs. These substances had reaction times typically of 1 to 10 seconds. ANEs, because of their slower reactive nature compared to the substances for which the test was developed, require 60 seconds or longer for any observable event. As discussed above the prolonged heating weakens the tube and thus any event in which the tube ruptures would be a false positive because of the weakened containment.

11. To ensure that the true substance reactivity is measured, as was the original intent of Koenen and Ide, it is proposed that the time during which the tube is heated be limited to 30 seconds, which is more than, albeit close to, the usable time of 25 seconds as specified by them.

## Proposals

### *Section 18*

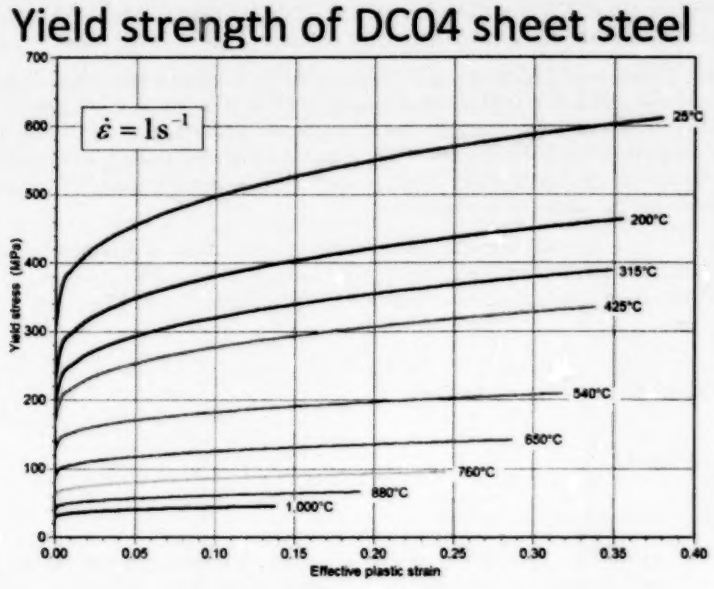
12. Amend 18.6.1.3.3 to read:

> 18.1.6.3.3 The tube is placed in a rigidly mounted vice and the nut tightened with a spanner. The tube is then suspended between the two rods in the protective box. The test area is vacated, the gas supply turned on and the burners lit. ~~The time to reaction and duration of reaction can provide additional information useful in interpreting the results.~~ If rupture of the tube does not occur within 30 seconds, heating is to be discontinued and the result of the test will be negative (-). ~~for at least five minutes before the trial is finished.~~ After each trial where rupture has occurred within 30 seconds the fragments of the tube~~, if any,~~ should be collected and weighed to ensure all pieces have been recovered.

## Consideration

13. For the purposes of Test Series 8, the present procedure with no time limitation on the Koenen test for ANEs results in false positives as the test is being applied to substances for which it was not designed and developed. AEISG and IME recommend that the Sub-Committee and its Working Group on Explosives give due consideration to accommodating the proposed time limit to ensure that that test assesses the behavior of the substance alone, and not that of the containing vessel as well. AEISG and IME believe that the proposed amendments are appropriate only for the Koenen Test found in Test Series 8 and are not submitted for consideration in other Koenen Tests found in Test Series 1, 2, and E.

## Appendix


Yield strength of DC04 sheet steel
$\dot{\varepsilon} = 1\,\mathrm{s}^{-1}$
Yield stress (MPa)
Effective plastic strain
25°C
200°C
315°C
425°C
540°C
650°C
760°C
880°C
1.000°C
0
100
200
300
400
500
600
700
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40